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(54) Ink/media combination

(57) An ink/media combination in which the ink comprises an aqueous medium, a colorant and an alginic acid salt selected from the group consisting of monovalent ion salts and organic amine salts and in which the media, preferably a textile, is treated with a specified water soluble salt of a metal having a valence of at least 2 produce printed chromatic image with improved bleed characteristics and sharper edges.

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Description

Background of the Invention

[0001] This invention relates to a ink and media combination in ink jet printing, and more particularly, to an ink/media combination that produces a chromatic and sharper edged image.

[0002] There are may methods of making printed elements in which printing liquids are applied to a substrate to form a image. The term "printing liquid", as it is commonly understood in the art, means a colorant in a liquid media, as distinguished from solid ad dry colorants, and includes paint, toners, inks, etc. The liquid media may be a organic solvent ("solvent based") or water ("aqueous based"). The colorant may be a dye or a pigment. Other ingredients typically are present in the printing liquid, depending upon the particular printing technique being employed.

[0003] Exemplary methods of using printing liquids include gravure and press printing, xerographic techniques using liquid toners, and ink jet printing, to name but a few. Of these methods, ink jet printing has become increasingly popular, particularly for so-called "desk-top publishing" applications, because of its ability to make multi-color prints by introducing three or four primary inks on a substrate in a single pass. Other printing methods generally require at least one pass through the printer for each primary color.

[0004] Despite the breadth of techniques available for making printed elements, a common problem can arise when a multi-colored element is desired in which a printing liquid of one color is placed in abutting relationship to a printing liquid of another color. This problem is manifested in a mixing or "bleeding" of the two printing liquids at their interface, whereby the line of demarcation between the two printing liquids is obscured. Bleeding may cause undesired color formation at the interface and a concurrent loss of resolution, color separation, edge acuity and color purity in the image. The more contrasting the two adjacent liquids are in color (such as black and yellow), the more visual the bleed. Bleed is also particularly noticeable when the mixing of two inks produces a secondary color, such as when blue and yellow mix to produce green.

[0005] Bleed is a particular problem in ink jet printing because the relatively low viscosity inks used therein tend to spread and because ink jet printers have the capability of printing three or four primary colors in simultaneous (or near simultaneous) fashion.

[0006] Several methods have been proposed to prevent bleed of adjacent printing liquids. The most obvious method is to apply the two printing liquids at a distance from one another such that no intermingling or mixing of the printing liquids can occur. This method is not a solution to the problem, however, and produces images having poor resolution.

[0007] Another method, and the one most commonly used, involves delay in applying the second printing liquid until the first printing liquid is completely dry. This method is also disadvantageous, not only because of its inefficiencies, but also because it is not particularly effective. For example, it has been observed that bleed may occur even if the first printing liquid is dry, which is believed to be caused by the colorants of the first printing liquid becoming "redissolved" in the liquid medium of the second printing liquid. Thus, the more soluble the components of the first printing liquid in the liquid medium, the more likely bleed will occur even if the first printing liquid is dry. This method is particularly disadvantageous in ink jet printing applications because it places an arbitrary limitation on the efficiency of generating multi-colored prints.

[0008] US Patent 5,091,005 teaches that the addition of formamide to the inks will reduce the occurrence of bleed in some circumstances. Yet another approach to control bleed is to increase the rate of penetration of the printing liquid into the substrate, which has its own shortcomings. First, it is inherently limited to those printing applications using particular printing liquid/substrate combinations. For example, highly absorbent substrates may be required to control bleed. Second, bleed will still be apparent unless the first printing liquid becomes bound to the substrate such that it will not be dissolved by the liquid medium of the second printing liquid. Third, known ways of increasing penetration have disadvantages in that they have a tendency to degrade text quality.

[0009] A combination of the above approaches is disclosed in US Patent 5,116,409, which discloses use of zwitterionic surfactants or non-ionic amphiphiles in concentrations above their respective critical micelle concentration. The formation of micelles containing dye molecules is said to prevent the dye molecules in each ink from mixing.

[0010] US Patent 5,181,045 teaches a method of ink jet printing wherein one of inks contains a dye that becomes insoluble under defined pH conditions and the other ink has a pH that renders the dye contained in the first ink insoluble. This method is inherently limited, however, to a specific group of dyes as colorants. In addition, the ink formulations are also constrained by the need for pH buffers, for example, which further limits the utility of that method.

[0011] EP 0586 079 A1 discloses a method for preventing color bleed between two different color ink compositions wherein the first ink is anionic and comprises a coloring agent which includes one or more carboxyl and/or carboxylate groups, and the second ink includes a precipitating agent which is designed to ionically crosslink with the coloring agent in the first ink to form a solid precipitate in order to prevent bleed between the two ink compositions. Multivalent metal salts are disclosed as being useful as the precipitating agent. Although this approach provides effective bleed contr l for two inks, it provides problems when more than two inks are applied to a printing medium in generating a multicolor

print. Further, this approach is very limiting because it does not allow for flexibility in the choice of coloring agent in the first ink which has to have one or more carboxyl and/or carboxylate groups capable of ionically bonding with the precipitating agent in the second ink.

[0012] Dyes are a common colorant used in ink jet printing due to their solubility in water. In addition, dyes provide vibrant chromatic colors on plain paper. Unfortunately, however, many dyes possess poor resistance to light, water and handling on paper. Consequently, dye colorants have deficiencies for archiving print samples.

[0013] Pigment colorants have been used as an alternative for dyes since they generally possess excellent light and water fastness. However, most pigments do not achieve the same color intensity (i.e., "chroma") on plain paper as dyes.

[0014] One approach to improve pigment chroma is to employ a vehicle that holds the colorant on the paper surface rather than allowing the pigment to diffuse into the printing media, e.g., fabric or paper. Such vehicles tend not to penetrate into the media, however, and are not adapted for quick drying or bleed control.

[0015] Accordingly, there is a need for an improved method for printing multi-colored images that does not present the bleed problem discussed above. Moreover, there is a particular need for such an improved method that achieves the favorable color chroma that may be obtained with dye colorants on media such as fabric, plain paper, etc., while providing the excellent resistance to water and light obtainable with pigment colorants. A specific need exists for such an ink/fabric combination that is capable of reproducing colored pictorial information which has sharply defined edges and no bleed of one color into another.

Summary of the Invention

[0016] The present invention provides an ink jet ink/media combination comprising:

(a) an ink comprising:

(1) an aqueous vehicle;
(2) a colorant; and
(3) 0.01 to 10% of an alginic acid salt selected from the group consisting of monovalent ion salts and organic amine salts; and

(b) a media treated with a water soluble salt comprised of a metal having a valence of at least 2.

[0017] The media is preferably fabric. The monovalent ion in the monovalent ion salt of alginic acid is selected from the group consisting of sodium, potassium, lithium and ammonium . Traces of calcium and magnesium salts may also be present in the alginic acid salt with no deleterious effects.

[0018] Preferably, the metal having a valence of at least 2 is selected from the group consisting of calcium, magnesium, aluminum, strontium, barium, zinc, stannous, stannic and copper.

[0019] The colorant may be a pigment or a dye. The ink/textile combination has general utility in printing, particularly in ink-jet printing applications using thermal or bubble jet printers, piezoelectric printers, continuous flow printers, air brush printers or valve jet printers.

Detailed Description of the Invention

[0020] The present invention provides an ink jet/media combination, preferably an ink jet ink/textile combination which provides printed images having improved line edge definition or reduced bleed in the imaged areas of the media. The essential components of the combination are the alginic acid salt in the ink and the water soluble salt of at metal having a valence of at least 2 (hereinafter the "metal +2 salt") in the media.

Media

[0021] The media may be any material capable of being treated or coated with the metal +2 salt, which may be applied to the media whereby it is absorbed into the media or it may be applied as a coating on the media. Some suitable media include textile, paper, transparent media such as polyethylene terephthalate films, etc. The preferred media is textile. Some useful textiles are selected from the group consisting of cellulose, fibrion hydroxy polymers, polyamide, polyesters, protein-like fibers polypropylene, polyacrylonitrile, cellulose triacetate and mixtures thereof. Preferably, the textiles contain hydroxy, amine, amido or carboxyl groups.

[0022] Examples of hydroxyl group containing textiles include, but are not limited to, cellulose containing fibers such as viscose staple and cotton. Suitable amine or amido group containing fibers include wool, synthetic polyamides and silk. Polyamide fibers include, but are not limited to, those spun from diamine-diacid polymers: nylon 6,6; nylon 6,12;

nylon 6,10 and nylon 4,6. Fibers spun from polymers derived from cyclic lactam monomers or omega-aminocarboxylic acids: Nylon 6, Nylon 7, Nylon 11, Nylon 12; and fibers spun from copolyamides of notably Nylon 6,6 or Nylon 6 are also included in this dye process. The copolyamides ref rred to above comprise a Nylon polymer f at least about 85% poly(hexamethylene adipamide), i.e., Nylon 6,6 units, or at least about 85% poly(epsilon-caproamide), i.e., Nylon 6 units. Suitable Nylon copolymers comprise at least about 85% Nylon 6,6 units with the balance being poly(hexamethylene isophthalamide) units, i.e., the polyamide product of isophthalic acid and hexamethylene diamine. Other copolymers useful in the practice of this invention include those having a varied diamine component. Suitable diamines include, but are not limited to the group consisting of: hexamethylene diamine, 2-methyl pentamethylene diamine, 2-ethyl tetramethylene diamine, meta-xylene diamine, and 1,4 bis-aminomethyl cyclohexane.

[0023] Some examples of carboxy group containing textile include, but are not limited to, polyester fibers such as thos based on polybutylene terephthalate, poly-1,4-cyclohexylene dimethylene terephthalate, but in particular polyethylene terephthalate, which may have been modified, for example, with the view to easier printability, by co-condensing them with other components such as other dicarboxylic acids and other diols.

[0024] Mixtures of these textiles are also considered within the invention. The finished form of the textile used to practic this invention includes, but is not limited to, fibers, yarns, fabrics, non-woven webs and garments, as well as, furnishings like carpets and upholstery fabrics.

Metal+2 Salt for Media Treatment:

[0025] Some suitable salts include calcium chloride, calcium bromide, calcium formate, calcium nitrate, strontium chloride, strontium bromide, strontium nitrate, barium actetate, barium bromide, barium chloride, barium propionate, copper chloride, copper nitrate, magnesium acetate, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, zinc acetate, zinc bromide, stannous sulfate, stannic sulfate, aluminum chloride, aluminum sulfate, aluminum nitrate, etc.

[0026] The metal +2 salt may be applied by conventional techniques known to those skilled in the art. Preferably, it is applied by padding. In this process, the media, e.g., fabric, is dipped in an aqueous solution of the metal +2 salt and excess liquid is removed from the media by squeegee rollers. On a small scale, the media may be dipped in the salt solution and the excess solution is allowed to drip off. Alternatively, the metal+2 salt may be coated on the media. Components such as binders, coating aids, etc. may be used to form the coating composition.

[0027] The amount of salt used may be in the range of 0.5 to 50%, preferably between 5 and 20%, based on the weight of the media.

Ink Composition

[0028] The ink comprises an aqueous vehicle, a colorant and an alginic acid salt. The alginic acid, when brought in contact with the metal+2 salt (with which the substrate has been treated), will coalescence the ink, thus reducing bleed. The ink also may contain other additives known in the art.

Aqueous Vehicle:

[0029] The aqueous vehicle is water or a mixture of water and at least one water-soluble organic solvent. Selection of a suitable mixture depends on requirements of the specific application, such as desired surface tension and viscosity, the selected colorant, drying time of the ink, and the type of substrate onto which the ink will be printed. Representative examples of water-soluble organic solvents that may be selected are disclosed in US Patent 5,085,698. A mixture of water and a polyhydric alcohol, such as diethylene glycol, is preferred as the aqueous vehicle.

[0030] If a mixture of water and a water-soluble solvent is used, the aqueous vehicle typically will contain 30% to about 95% water with the balance (i.e., 70 to 5%) being the water-soluble solvent. Preferred compositions contain approximately 60% to 95% water, based on the total weight of the aqueous vehicle.

[0031] The amount of aqueous vehicle in the ink is in the range of approximately 70 to 99.8%, preferably 80 to 99.8%, based on total weight of the ink when an organic pigment is selected; approximately 25 to 99.8%, preferably 70 to 99.8% when an inorganic pigment is selected; and 70 to 99.8% when a dye is selected.

Colorant:

[0032] The colorant may be a dye or a pigment. Pigments are particularly preferred.

Dyes

[0033] As used herein, th term "dye" means a colorant that, at s me point in th printing process, becomes soluble. The term includes both dyes that are soluble in the aqueous vehicle and those that are not soluble in the aqueous vehicle under normal formulation conditions. Dyes in this latter category are also known as dispersed dyes.
[0034] Dyes useful in this invention include anionic, amphoteric and non-ionic dyes. Such dyes are well known in the art. Anionic dyes yield colored anions in aqueous solution. Typically anionic dyes contain carboxylic or sulfonic acid groups as the ionic moiety and encompass all acid dyes.
[0035] The types of anionic dyes most useful in this invention are Acid, Direct, Food, Mordant, and Reactive dyes. Anionic dyes are nitroso compounds, nitro compounds, azo compounds, stilbene compounds, triarylmethane compounds, xanthene compounds, quinoline compounds, thiazole compounds, azine compounds, oxazine compounds, thiazine compounds, aminoketone compounds, anthraquinone compounds, indigoid compounds and phthalocyanine compounds.
[0036] The color and amount of dye used in the ink composition is largely a function of choice, being primarily dependent upon the desired color of the print achieved with the ink, the purity of the dye and its strength. Low concentrations of dye may not give adequate color vividness. High concentrations may result in poor printhead performance or unacceptably dark colors. The dye is present in the amount of 0.01 to 20%, by weight, preferably 0.05 to 8%, by weight, more preferably 1 to 5%, by weight, based on the total weight of the ink.

Pigment

[0037] The term "pigment" as used herein means a colorant that remains in a crystalline or particulate state throughout the printing process. Organic or inorganic pigments may be selected, alone or in combination. Organic pigments having functional groups (e.g., acid, base, epoxy, and hydroxy groups) that will react with a media component may be selected to advantage in particular applications.
[0038] The pigment particles are sufficiently small to permit free flow of the ink through the ink jet printing device, especially at the ejecting nozzles that usually have a diameter ranging from 10 micron to 50 micron. The particle size also has a influence on the pigment dispersion stability, which is critical throughout the life of the ink. Brownian motion of minute particles will help prevent the particles from settling. It is also desirable to use small particles for maximum color strength. The range of useful particle size is approximately 0.005 micron to 15 micron. Preferably, the pigment particle size should range from 0.005 to 5 micron and most preferably, from 0.01 to 0.3 micron.
[0039] The selected pigment may be used in dry or wet form. Pigments are usually manufactured in aqueous media and the resulting pigment is obtained as water wet presscake. In presscake form, the pigment is not aggregated to the extent that it is in dry form. Thus, pigments in water wet presscake form do not require as much deaggregation in the process of preparing the inks from dry pigments. Representative commercial dry and presscake pigments that may be used to advantage are disclosed in US Patent 5,085,698.
[0040] Fine particles of metal or metal oxides also may be used to practice the invention. For example, metal and metal oxides are suitable for the preparation of magnetic ink jet inks. Fine particle size oxides, such as silica, alumina, titania, and the like, also may be selected. Furthermore, finely divided metal particles, such as copper, iron, steel, aluminum and alloys, may be selected for appropriate applications.
[0041] When an organic pigment is selected, the ink may contain up to approximately 30% pigment by weight, but typically will be in the range of 0.1 to 15% (preferably 0.1 to 8%) by weight for most thermal ink jet printing applications. If an inorganic pigment is selected, the ink will tend to contain higher weight percentages of pigment than with comparable inks employing organic pigment, and may be as high as approximately 75% in some cases, because inorganic pigments generally have higher specific gravity than organic pigments.
[0042] Typically the use of a pigment (or a dispersed dye) as a colorant will require a dispersant or surfactant to help maintain the insoluble colorant in the aqueous vehicle. Polymeric dispersants are the dispersant of choice for most applications, particularly structured polymeric dispersants.

Polymer:

[0043] In the preferred embodiment, the ink will contain a polymer. The polymer may function as a dispersant for the insoluble colorant (i.e., pigment or dispersed dye) or as a binder. Preferably the polymer will be a structured polymer such as an AB or BAB block copolymers (*see e.g.*, US Patent 5,085,698), ABC triblock copolymers (*see e.g.*, European Patent Application 0 556 649 A1), or a branched or graft polymer (*see e.g.*, US Patent 5,231,131).
[0044] Although random copolymers can be used as dispersing agents, they are not as effective in stabilizing pigment dispersions as the structured polymers, and therefore are not preferred. Useful random interpolymers have narrowly controlled molecular weight ranges preferably having poly dispersivities of 1.3, preferably 1.2. These polymers are sub-

stantially free of higher molecular weight species that readily plug pen nozzles. Number average molecular weight must be less than 10,000 Daltons, preferably less than 6,000, most preferably less than 3,000. The random polymers contain hydrophobic and hydrophilic monomer units. Commercial random dispersant polymers will plug pen nozzles readily. However, needed molecular weight control can be obtained by using the Group Transfer Polymerization technique, or other methods that deliver low dispersivity. Some examples of hydrophobic monomers used in random polymers are methyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, 2-phenylethyl methacrylate and the corresponding acrylates. Examples of hydrophilic monomers are methacrylic acid, acrylic acid, dimethylaminoethyl [meth]acrylate and salts thereof.

[0045] Polymeric binder additives, especially ones with crosslinkable moieties, such as acid, hydroxy, amine, etc. can be included in the ink formulation. These can be of various types such as linear, emulsion, including core shell and emulsions stabilized by structured polymers, hydrosols, etc.

Salt of Alginic Acid

[0046] The salt of alginic acid is a monovalent ion salt or an organic amine salt. The monovalent ion is selected from the group consisting of sodium, potassium, lithium and ammonium. Traces of calcium and magnesium salts may also be present in the alginic acid salt with no deleterious effects. Some useful organic amines include methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine and triethyl amine.

[0047] Alginate salts are manufactured from the natural product algin. Algins are prepared from brown seaweed by a complex extraction process. There are a number of species of brown algae. Macrocystis pyrifera is the primary commercial source of algin. Other species are ascophyllum nodosum, laminaria digitata, laminaria hyperborea, ecklonia cava, and eisenia bicyclis. The algin polymer is made up of D-Mannuronic acid and L-Guluronic acid residues in about a 60:40 ratio. The polymer is thought to contain three types of segments: a polymannuronic acid segment, a polyguluronic acid segment, and an alternating unit segment. The algin from macrocystis pyrifera contains these segments in about a ratio of 40:20:40. The polyguluronic acid segments are thought to associate with the divalent or trivalent ions to link polymer chains. The preferred alginate salts are primarily sodium salts as manufactured, but may also contain small amounts of potassium, calcium, and magnesium.

Other Ingredients:

[0048] Consistent with the particular application, various types of additives may be used to modify the properties of the ink composition. Anionic, nonionic, or amphoteric surfactants may be used in addition to the polymeric dispersants. A detailed list of non-polymeric as well as some polymeric surfactants are listed at pages 110-129, of 1990 McCutcheon's Functional Materials, North America Edition, Manufacturing Confection Publishing Co., Glen Rock, NJ. The choice of a specific surfactant is highly dependent on the particular ink composition and type of textile to be printed. One skilled in the art can select the appropriate surfactant for the specific substrate to be used in the particular ink composition. In aqueous inks, the surfactants may be present in the amount of 0.01-5% and preferably 0.2-2%, based on the total weight of the ink.

[0049] Cosolvents may be included to improve penetration and pluggage inhibition properties of the ink composition, and in fact are preferred. Such cosolvents are well known in the art. Representative cosolvents that can be used to advantage are exemplified in US 5,272,201. Biocides may be used to inhibit growth of microorganisms. Dowicides® (Dow Chemical, Midland, MI), Nuosept® (Huls America, Inc., Piscataway, NJ), Omidines® (Olin Corp., Cheshire, CT), Nopcocides® (Henkel Corp., Ambler, PA), Troysans® (Troy Chemical Corp., Newark, NJ) and sodium benzoate are examples of such biocides. Sequestering agents such as EDTA may also be included to eliminate deleterious effects of heavy metal impurities. Other known additives, such as humectants, viscosity modifiers and other acrylic or non-acrylic polymers may also be added to improve various properties of the ink compositions as desired.

Ink Properties

[0050] Jet velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the ink. Pigmented ink jet inks suitable for use with ink jet printing systems should have a surface tension in the range of about 20 dyne/cm to about 70 dyne/cm and, more preferably, in the range 30 dyne/cm to about 70 dyne/cm at 20°C. Acceptable viscosities are no greater than 20 cP, and preferably in the range of about 1.0 cP to about 10.0 cP at 20°C. The ink has physical properties compatible with a wide range of ejecting conditions, i.e., driving voltage and pulse width for thermal ink jet printing devices, driving frequency of the piezo element for either a drop-on-demand device or a continuous device, and the shape and size of the nozzle. The inks have excellent storage stability for a long period ad do not clog in an ink jet apparatus. Fixing of the ink on the media having th appropriate treatment thereon, can be carried out speedily and surely. The printed ink images have clear color tones and high. Fur-

ther, the ink does not corrode parts of the ink jet printing device it comes in contact with, and it is essentially odorless, and non-toxic.

Applications

[0051] The ink is applied to the textile using conventional techniques such as thermal or bubble jet printers, piezoelectric printers, continuous flow printers, air brush or valve jet printers. After the ink is printed on the textile, the printed textile is air dried.

Examples

[0052] In the examples following, parts and percentages are by weight unless otherwise noted.

[0053] **Example 1** Two inks were prepared. Ink A contained 1% Direct Blue 199 (Organic Dyestuffs Corp., East Providence, RI)), 20% trimethylolpropane, and 0.25% sodium alginate in water. Ink: C, the comparison ink, was of the same composition, except the alginate was omitted. The fabric, 90 g/M^2 silk Charmeuse, was designated as S. This fabric was treated by soaking in a 5% calcium chloride solution and drying. The treated fabric was designated 'ST'.

[0054] The ink was loaded into a recycled HP 51626A cartridge. Blocks of solid color were printed on the fabric using an HP DeskJet 550C printer (Hewlett-Packard Co., Palo Alto, CA.) The color chroma C* and lightness L* was determined for each sample. The color saturation s* was calculated from C* and L*. The Kubelka Munk k/s was determined for the maximum absorbance. Color strength was calculated by the sample k/s divided by the k/s for the ink/fabric combination containing no additive. 'Much' bleed is defined as ink wicking along the fiber 1 mm beyond the printed area. 'None' means no bleed was seen with a 10X magnifying glass. 'Medium' bleed is a intermediate level of ink wicking between 'Much' and 'None'. Results are shown in Table 1 below.

TABLE 1

Sample #	Ink	Fabric	Bleed	C*	s*	k/s	Color Strength
1	A	ST	none	45.4	0.72	2.80	147%
2 (Control)	A	S	medium	37.8	0.55	1.91	101%
3 (Control)	C	ST	medium	42.2	0.66	2.41	127%
4 (Control)	C	S	much	37.0	0.54	1.90	100%

[0055] This data shows that Sample 1 containing both the alginate in the ink and the salt in the fabric are needed for the full effect. It shows the color strength is substantially improved by the alginate and salt combination.

Comparative Example 1

[0056] Example 1 was repeated with the following exception: a 5% solution of sodium chloride or potassium chloride solution was used to treat the silk fabric instead of the 5% solution of calcium chloride. Results are shown in Table 2 below.

TABLE 2

Sample #	Fabric Treatment	Weight Gain (%)	Ink	C*	s*	k/s	Color Strength
1	none	0.0	A	38.0	0.56	2.08	100%
2	NaCl	12.2	A	38.3	0.57	2.33	112%
3	NaCl	12.5	A	37.7	0.56	2.37	114%
4	none	0.0	C	36.4	0.54	2.10	100%
5	KCl	10.6	C	37.4	0.56	2.18	104%
6	KCl	10.7	C	37.7	0.56	2.20	105%

[0057] This exampl shows there is no effect on the color strength when a monovalent salt is used to treat the fabric with or with ut alginate in the

Example 2

[0058] Example 1 was repeated with the following exception: a 107 g/M^2 worsted wool Challis, designated as 'OWO', was used in place of the silk. The treated fabric was designated as 'OWTO'. Results are shown in Table 3 below:

TABLE 3

Sample #	Ink	Fabric	C*	s*	k/s	Color Strength
1	A	OWTO	39.3	0.65	3.61	138%
2 (Control)	A	OWO	38.0	0.61	3.20	122%
3 (Control)	C	OWTO	38.4	O.64	3.44	131%
4 (Control)	C	OWO	35.5	0.56	2.62	100%

[0059] As in Example 1, this shows both alginate and salt are needed to give the highest color chroma and strength.

Example 3

[0060] Pieces of silk S, similar to that used in Example 1, were soaked in calcium chloride solutions at various concentrations. After these were dried, the weight gain was determined for each piece. The pieces were printed with Ink A as in Example 1. Bleed and color strength were measured as in Example 1. Results are shown in Table 4 below:

TABLE 4

Sample#	$CaCl_2$ (%)	Weight Gain (%)	Bleed	C*	s*	k/s	Color Strength
1(Control)	none	0.0	much	35.3	0.51	1.83	100%
2	0.1	0.75	medium	40.5	0.61	2.78	151%
3	0.5	1.35	slight	41.5	0.62	2.70	147%
4	1.0	2.86	slight	43.0	0.66	3.00	164%
5	5.0	14.04	none	44.8	0.70	3.50	191%
6	10.0	28.27	none	43.9	0.67	3.17	173%
7	20.0	*	*	*	*	*	*

* Sample never dried

[0061] This data shows that a wide range of amounts of the calcium chloride solution can be used to treat the fabric resulting in reduced bleed and increased color yield.

Example 4

[0062] Pieces of silk S, similar to that used in Example 1 were soaked in 5% solutions of various salts. After drying, the weight gain was determined for each piece of silk. The pieces were printed with ink A as in Example 1. Bleed and color strength were measured as in Example 1. Results are shown in Table 5 below:

TABLE 5

Sample#	Fabric Treatment (5% Soln.)	Weight Gain (%)	Bleed	C*	s*	k/s	Color Strength
1 (Control)	none	0.0	much	39.4	0.59	2.29	100%
2	$MgCl_2$	9.6	none	40.4	0.63	2.80	122%
3	$SrCl_2$	9.6	none	44.9	0.70	3.80	166%
4	$BaCl_2$	12.3	none	44.6	0.70	4.00	175%
5	$AlNO_4$	9.2	none	40.5	0.62	3.19	139%
6	$CaCl_2$	8.4	none	44.4	0.71	3.89	170%

[0063] This data shows that any one of a number of divalent or trivalent salts can be used in this invention to give printed images with increased color strength and reduced bleed.

Claims

1. An ink jet ink/media combination comprising:

   (a) an ink comprising:

      (1) an aqueous vehicle;
      (2) a colorant; and
      (3) 0.01 to 10% of an alginic acid salt selected from the group consisting of monovalent ion salts and organic amine salts; and

   (b) a media treated with a water soluble salt comprised of a metal having a valence of at least 2.

2. The ink/media combination of Claim 1 wherein the media is a texile.

3. The ink/media combination of Claim 2 wherein the alginic acid salt comprises is a monovalent ion salt wherein the monovalent ion is selected from the group consisting of sodium, potassium, lithium and ammonium.

4. The ink/media combination of Claim 2 wherein the alginic acid salt is an organic amine salt wherein the organic amine is selected from the group consisting methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine and triethyl amine.

5. The ink/media combination of Claim 2 wherein the water-soluble salt is selected from the group consisting of calcium chloride, calcium bromide, calcium formate, calcium nitrate, strontium chloride, strontium bromide, strontium nitrate, barium acetate, barium chloride, barium bromide, barium propionate, copper chloride, copper nitrate, magnesium acetate, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, zinc acetate, zinc bromide, zinc chloride, zinc nitrate, zinc phosphate, zinc sulfate, stannous sulfate, stannic sulfate, aluminum chloride, aluminum sulfate and aluminum nitrate.

6. The ink/media combination of Claim 2 wherein the ink further contains a polymer.

7. The ink/media combination of Claim 6 wherein the polymer is a dispersant and wherein the colorant is a pigment.

8. The ink/media combination of Claim 6 wherein the polymer is a structured polymer.

9. The ink/media combination of Claim 2 wherein the colorant comprises a dye.

10. The ink/media combination of Claim 2 wherein the textile is selected from the group consisting of silk and wool.